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Density Functional Theory Investigation of Bond Length, Bond Angle and Thermodynamic Parameters in 4-Amino-2-Hydroxy-6-Phenylpyrimidine-5 Carboxamide

J. S. Aher*[,1], A. V. Kardel[2], M. R. Gaware[3], D. D. Lokhande[3], A. M. Bhagare[4]

[1]Department of Chemistry, K.R.T. Arts, B.H. Commerce and A. M. Science College, Shivaji Nagar, Gangapur Road Nashik 422 002, Maharashtra, India.

[2]Department of Chemistry, KGDM Arts, Commerce and Science College, Niphad, 422 303 Dist. Nashik, Maharashtra, India.

[3] Department of Chemistry, KPG Arts, Commerce and Science College Igatpuri, 422 402, Dist. Nashik, Maharashtra, India.

[4]Department of Chemistry, Arts, Commerce and Science College, Pimpalgaon (B.) 422 209, Dist. Nashik, Maharashtra, India.

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***Corresponding author E-mail address:** *js_aher@rediffmail.com*

ABSTRACT

Theoretical chemistry method has been adopted to correlate the structural and electronic properties such as bond length, bond angle, Mullikan's charges, HOMO-LUMO energy values, energy gap, dipole moment (μ), electron affinity(A), ionization potential (I), electronegativity (χ), global hardness (η), softness(σ), electrophilicity index (ω) and thermodynamic parameters are using density functional theory (DFT) at the B3LYP/6-311 G ++ (d, p) basis set of 4-amino-2-hydroxy-6-phenylpyrimidine-5-carboxamide.

KEYWORDS

DFT, HOMO-LUMO, dipole moment, energy gap, thermodynamic parameter.

1. INTRODUCTION

Density Functional Theory (DFT) is a method used to investigate Quantum chemical calculation of energies, geometrical structure and vibrational wave numbers of 4-amino-2-hydroxy-6-phenylpyrimidine-5-carboxamide. The optimized geometrical parameters obtained by DFT calculations. Using a theory many properties can be evaluated using functional that is functions of another. Application of density functional theory to UV, IR and NMR spectroscopic study gives clear interpretations λmax values, modes of vibrations, vibrational frequencies, coupling constant etc. The vibrational spectral data obtained from solid phase FT-IR and ^{1}H NMR is assigned to base on the results of the theoretical calculations. The observed spectra are found to be in good agreement with calculated values. Pyrimidines are important heterocyclic moiety in many organic compounds and contributed due importance in pharmacological applications [1], biological uses [2-8], herbicidal effects [9], pesticides impact [10], synthetically applications [11], polymeric and material sciences [12]. Many researchers have reported the *ab initio* Hartree-Fock calculations and DFT study of different heterocyclic compounds [13-16].

In the present work, we have correlated experimental and theoretical IR and NMR spectrum along with molecular structure of 4-amino-2-hydroxy-6-phenylpyrimidine-5-carboxamide investigated by determining the chemical indexes using density functional theory (DFT) at the B3LYP/6-311++G (d, p) level. To the best of our knowledge, the structural and thermodynamic parameters of this compound have not been reported earlier in open literature.

2. MATERIALS AND METHODS

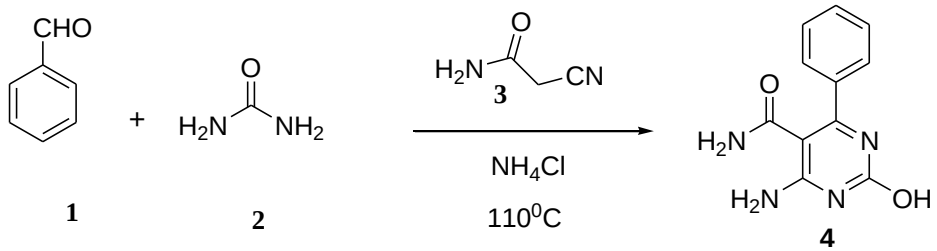
2.1. Chemicals

The reagents required for synthesis of 4-amono-2-hydroxy-6-phenylpyrimidine-5-carboxamide has analytical grade purchased from Sigma Aldrich and S.D. fine chemicals and are used without further purification. The melting points have recorded on open capillary method and are uncorrected. .IR spectrum has recorded as KBr pellets on a Shimadzu FTIR-408 spectrophotometer. The ^{1}H-NMR spectrums are recorded on Bruker 500 MHz, NMR spectrometer using CDCl3 as solvent.

2.2. Methods

2. 2.1 Synthesis of 4-amono-2-hydroxy-6-phenylpyrimidine-5-carboxamide

The 4-amino-2-mercapto-6-phenylpyrimidine-5-carboxamide (4) has synthesized from one pot synthesis of aldehyde (1), urea (2) and cyanoacetamide (3), in presence of ammonium chloride under solvent free condition by following scheme-1.



Scheme I

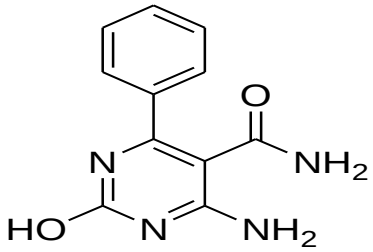
2.2.2. Computational details

The Computational calculations had performed on Lenovo, Core i3 personal computer using the Gaussian 09 program package. Geometries of the molecules have optimized by DFT/B3LYP at 6-311++G (d, p) as basis set. The optimized geometry parameters have used to confirm the structure as minima. Gauss View 5.0 molecular visualization program has used for HOMO, LUMO plots and energy has used to calculate absorption maxima and the chemical reactivity of the molecule.

2.2.3. Spectral Data

The experimental and theoretical data has shown below. The experimental IR and 1H-NMR spectral data of the compound are list in table 1. While experimental and theoretical IR and ^{1}H-NMR spectrum has shown in Fig. 1 to Fig. 4 respectively.

Table 1. Experimental and theoretical spectral data of 4-amono-2-hydroxy-6-phenylpyrimidine-5-carboxamide.

	**Experimental Data**	**Theoretical Data**
IR data Cm-1	3396 OH str.	3795 OH str.
	3350 N-H Str.	3518 N-H str.
	3157 Ar-H str.	3199 Ar-H str.
	1689 C=O str.	1699 C=O str.
	1492 Ar C=C	1640 Ar C=C str.
	1595 C=N str	1596 C=N str.
1H NMR δ (ppm) at 500 MHZ DMSO	8.19 (1H, S-OH)	H8-8.14
	7.95 (2H, S- NH2)	H9-7.67
	7..93-7.56 (5H, m Ar-H)	H7-7.62
		H10-7.56
		H6-7.46
		H27-8.27 (N-H)
		H26-4.80 (N-H)
		H21-5.32 (O-H)
		H23-4.47 (CO-NH2)
		H24-4.38 (CO-NH2)

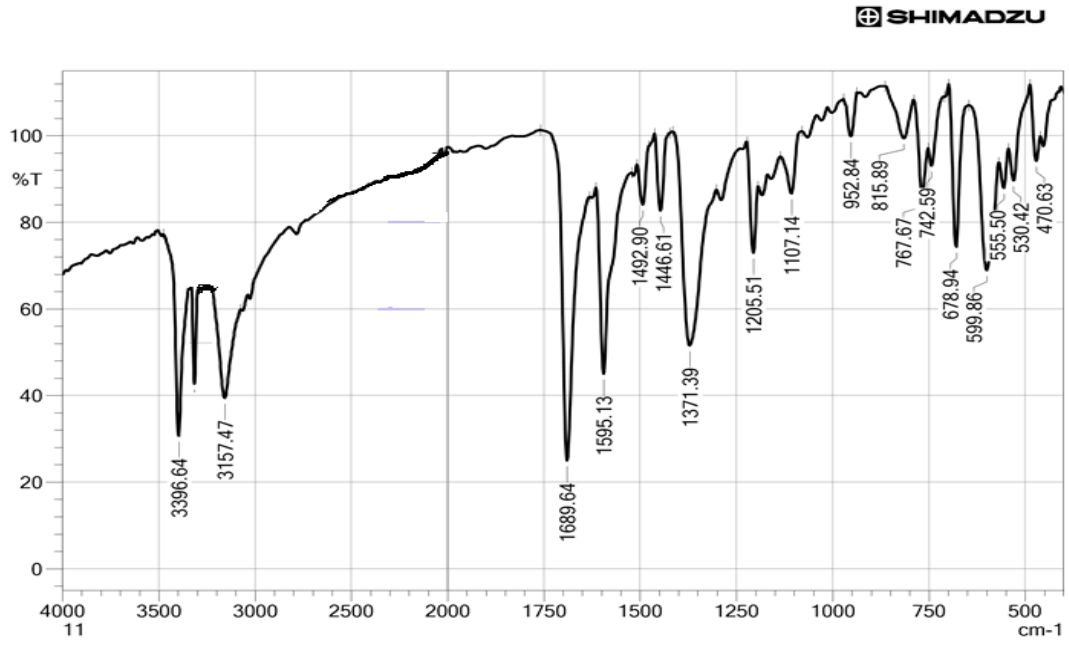


Fig. 1. IR spectrum of 4-amino-2-hydroxy-6-phenylpyrimidine-5-carboxamide.

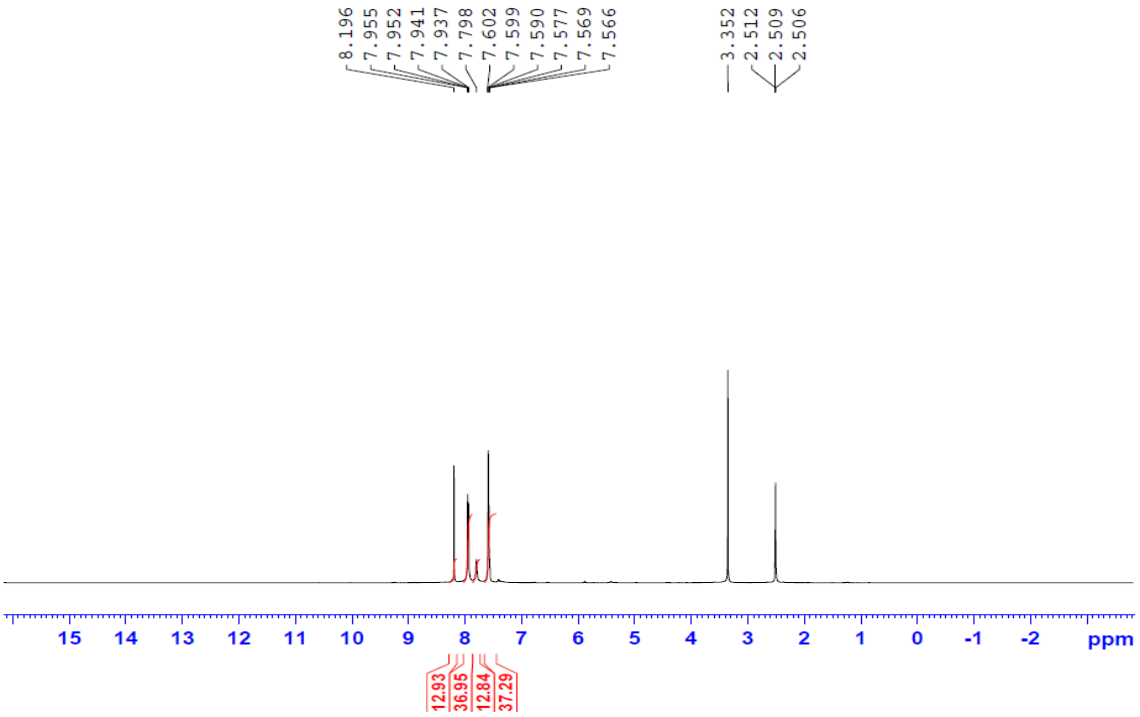


Fig. 2. H[1]NMR spectrum of 4-amino-2-hydroxy-6-phenylpyrimidine-5-carboxamide.

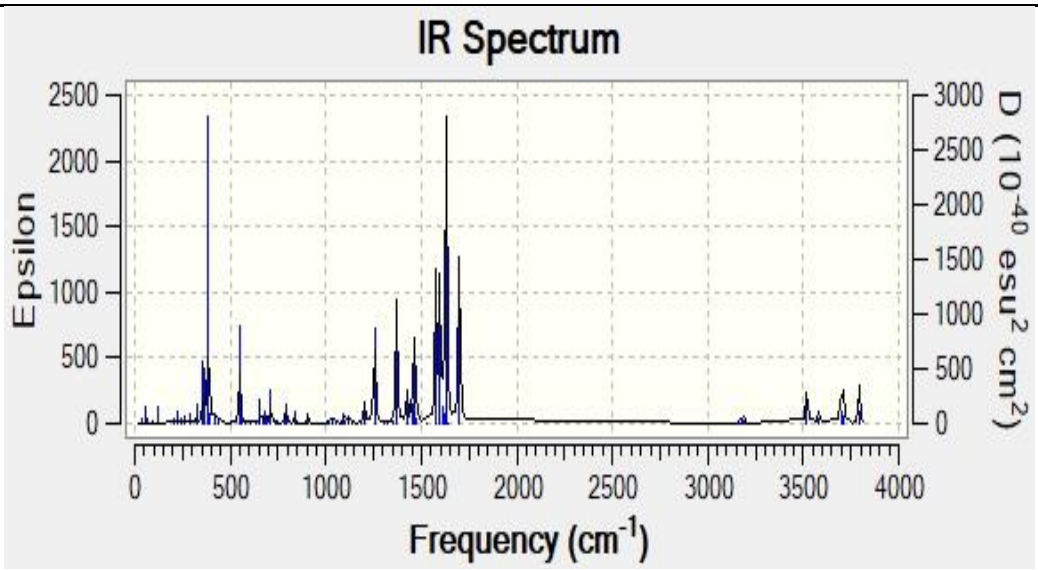


Fig. 3. IR spectrum of4-amino-2-hydroxy-6-phenylpyrimidine-5-carboxamide.

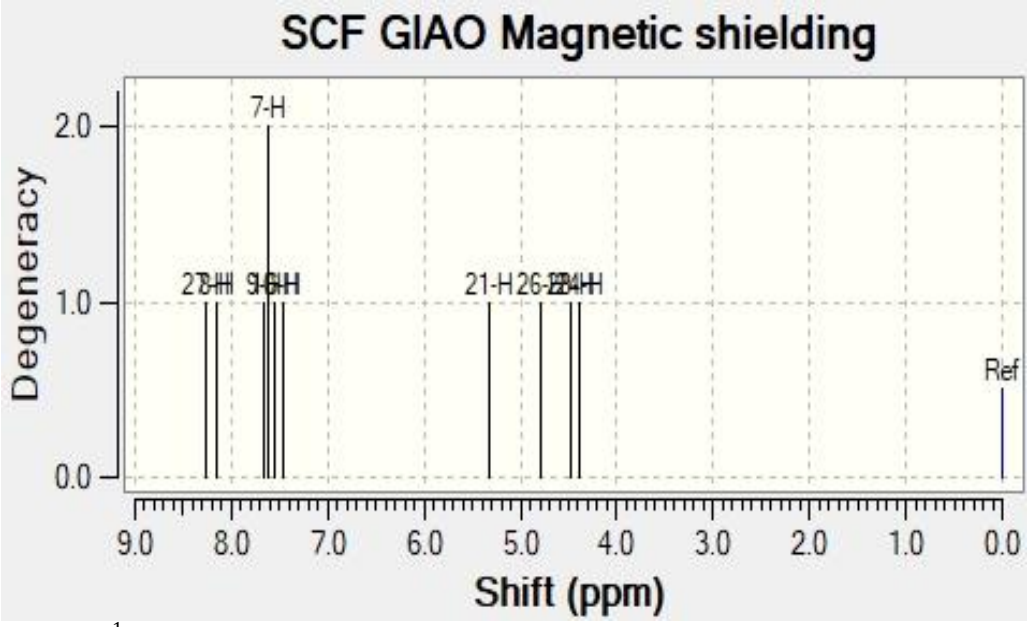


Fig. 4. H[1]NMR spectrum of 4-amino-2-hydroxy-6-phenylpyrimidine-5-carboxamide.

3. RESULTS AND DISCUSSION

Molecular geometry: The optimized geometrical parameters (bond length, bond angles) have listed in Table 2 and Table 3 respectively according to numbering reported in optimized structure of titled compound. C1 point group symmetry has showed the planner structure of titled compound. There are 27 atoms in the molecule of titled compound, so 75 normal modes of

fundamental vibrations are expected. Slight variation has been observed in experimental and theoretical IR and 1HNMR data for the said compound. For better up gradation across agreement between observed and calculated vibrational frequencies, calculated absorption frequencies have adjusted by multiplying with scaling factor 0.9631 for density functional theory resulting in computed absorption frequencies. The scaled vibrational frequencies are listed in table 1.

3.1. C=O stretching vibrations

The open chain simple carbonyl from 10 amide group (H2N-C=O) absorbs within the range 1640-1700 cm^{-1}. The computed stretching frequency of carbonyl in amide group for the compound is at 1699 cm^{-1}.While the experimental stretching frequency of carbonyl in amide group for the compound is at 1689 cm^{-1}.

3.2. C=C stretching vibrations

Aromatic C=C stretching is observed in the range between 1585-1600 and 1450-1500 cm^{-1}. The computed stretching frequency of aromatic C=C stretching absorption bands is observed at 1640 cm^{-1}. While experimental aromatic C=C starching observed at 1492 cm^{-1}.

3.3. N-H vibration

1^0 amides shows N-H stretching observed in the range between 3300- 3500 cm^{-1}. The computed stretching frequency has observed at 3518 cm^{-1}.While experimental stretching frequency has observed at 3350 cm^{-1}.

3.4. O-H stretching vibration

Stretching frequency of O-H has observed in range between 3400-3200cm^{-1}very broad.

The computed stretching frequency has observed at 3795 cm^{-1}. While experimental stretching frequency has observed at 3396 cm-1.

4. OPTIMIZED STRUCTURE

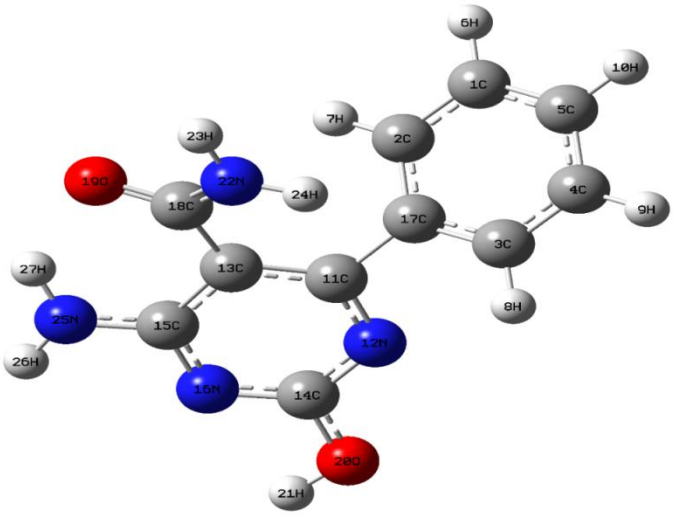


Fig. 2. Optimized Structure of 4-amino-2-hydroxy-6-phenylpyrimidine-5-carboxamide

4.1. Bond lengths

Table 2. Optimized bond lengths (A^0) of 4-amino-2-hydroxy-6-phenylpyrimidine-5-carboxamide by DFT method at B3LYP level using 6-311++G (d, p) as basis sets.

Atoms	Bond lengths (A^0)	Atoms	Bond lengths (A^0)
C1-C2	1.3921	C11-C17	1.4918
C1-C5	1.3947	N12-C14	1.3267
C1-H6	1.0841	C13-C15	1.4345
C2-H7	1.084	C13-C18	1.4932
C2-C17	1.401	C14-N16	1.3256
C2-N22	3.1569	C14-O20	1.3441
C3-C4	1.3923	C15-N16	1.3443
C3-H8	1.083	C15-N25	1.3447
C3-C17	1.401	C18-O19	1.2338
C4-C5	1.3944	C18-N22	1.3615
C4-H9	1.0841	O20-H21	0.9668
C5-H10	1.0842	N22-H23	1.0085
H7-N22	3.1276	N22-H24	1.0066
C11-N12	1.342	N25-H26	1.0065
C11-C13	1.4061	N25-H27	1.0127

4.2. Bond Angles

Table 3. Optimized bond angles of 4-amino-2-hydroxy-6-phenylpyrimidine-5-carboxamide by DFT method at B3LYP level using 6-311++G (d, p) as basis sets.

Atoms	Bond Angles	Atoms	Bond Angles
C2-C1-C5	120.1463	N12-C14-O20	115.391
C2-C1-H6	119.7187	N16-C14-O20	116.733
C5-C1-H6	120.1339	C13-C15-N16	121.0662
C1-C2-H7	119.8347	C13-C15-N25	122.4286
C1-C2-C17	120.3921	N16-C15-N25	116.4915
C1-C2-N22	120.7994	C14-N16-C15	116.6735
H7-C2-C17	119.7625	C2-C17-C3	119.1025
C17-C2-N22	72.5731	C2-C17-C11	121.2737
C4-C3-H8	120.6005	C3-C17-C11	119.5161
C4-C3-C17	120.3837	C13-C18-O19	121.7966
H8-C3-C17	119.0127	C13-C18-N22	117.9162
C3-C4-C5	120.1467	O19-C18-N22	120.102
C3-C4-H9	119.7451	C14-O20-H21	106.7587
C5-C4-H9	120.1037	C2-N22-C18	82.6569
C1-C5-C4	119.8041	C2-N22-H23	117.1916

C1-C5-H10	120.0671	C2-N22-H24	58.4677
C4-C5-H10	120.1256	H7-N22-C18	68.2698
N12-C11-C13	122.5212	H7-N22-H23	110.3618
N12-C11-C17	113.6764	H7-N22-H24	78.3084
C13-C11-C17	123.76	C18-N22-H23	116.7582
C11-N12-C14	116.0021	C18-N22-H24	122.3141
C11-C13-C15	115.2623	H23-N22-H24	118.4762
C11-C13-C18	126.4437	C15-N25-H26	117.9466
C15-C13-C18	118.2337	C15-N25-H27	118.6433
N12-C14-N16	127.8597	H26-N25-H27	122.4604

4.3. Mullikan Atomic Charges

Atomic charges play an important role in the application of quantum chemical calculations to molecular system. It has used to get information on the electron densities of the atoms. Atomic charges have obtained using the Natural Population Analysis (NPA) based on the DFT /B3LYP/6-311++G (d, p) as basis set and has listed in table 4.More positive charge has found to present on C17 (0.721602) and more negative charge is present onC2 (-0.758026).

Table 4. Computed Mullikan Atomic Charges (a. u) by NPA calculated by DFT at B3LYP / 6-311++G (d, p) as basis set.

Atoms	Charges	Atoms	Charges
C1	-0.323442	C15	-0.029961
C2	-0.758026	N16	-0.208248
C3	0.088486	C17	0.721602
C4	-0.305073	C18	-0.396754
C5	-0.250921	O19	-0.358165
H6	0.186281	O20	-0.194737
H7	0.191859	H21	0.308484
H8	0.210930	N22	-0.366366
H9	0.180641	H23	0.310463
H10	0.156103	H24	0.284867
C11	-0.280325	N25	-0.379579
N12	-0.085226	H26	0.297707
C13	0.398802	H 27	0.317488
C14	0.283109	-	-

4.4. HOMO-LUMO energy and absorption maxima

The Highest Occupied Molecular Orbital (HOMO) that can act as an electron donor and the Lowest Unoccupied Molecular Orbital (LUMO) that can accept electron. HOMO-LUMO energy

gap can be used to predict the absorption maxima (λmax) of the molecule [17] by using following equations [18]. Energy gap (eV) = Energy gap (Hartree or a.u.) x 27.2113834
λmax= 1240/Energy gap (eV) ---Equation 1
For the compound HOMO-LUMO energy and λmax are calculated and has found at 256.641 nm as shown in table 5.

4.5. Chemical reactivity indices

The chemical reactivity indices such as total energy (E), global chemical hardness (Ƞ), global chemical softness (σ), electronic chemical potential (μ), electronegativity (χ) and electrophilicity index (ω) is being calculated by using HOMO-LUMO energy gap and which provides information about reactivity of molecule. The values of all these indices are listed in table 5.

4.6. Global chemical hardness (Ƞ)

It is associated with the stability and reactivity of the chemical system. It measures the resistance to change in the electron distribution or charge transfer. Chemical hardness is calculated using following equation. Global chemical Softness (**σ)** is the reciprocal of global chemical hardness given by the equation,
((E LUMO - E HOMO))/2. ---Equation 2

Where, ELUMO and EHOMO are the LUMO and HOMO energies. The larger the HOMO-LUMO energy gap, the harder and more stable/less reactive the molecule.

4.7. Electronegativity (χ)

Pauling [19] put the concept of electronegativity forward. It is the power of an atom in a molecule to attract electrons towards it. Higher is the electronegativity of the species, greater is its electron accepting power and greater is the electrophilicity. It has determined by using following equation,
(E LUMO + E HOMO)/2. ---Equation 3

4.8. Electronic chemical potential (μ)

It describes the escaping tendency of electrons from an equilibrium system and is same in magnitude to that of the electronegativity with opposite sign or half of the sum of HOMO and LUMO energy and it has determined using equation. (E LUMO + E HOMO)/2. Greater the electronic chemical potential, less stable or more reactive is the compound.

4.9. Global electrophilicity index (ω)

It has introduced by Paar and measure of the capacity or propensity of a chemical species to accept electrons and stabilization in energy when chemical system accepts additional amount of electronic charge from the environment. Global electrophilicity index hascalculated by using the electronic chemical potential and chemical hardness by following equation,
$\omega=\mu^2/2\ \eta$ ---Equation 4

4.10. Ionization energy (I) and electron affinity (A)

The Gas phase ionization energies (I) and electron affinities (A) of the isomers have related to the HOMO and LUMO energies according to the Koopmans' theorem by the following equation, A= -E LUMO and I= - E HOMO ---Equation 5

Electron affinity is the capability of a ligand to accept precisely one electron from a donor.

Table 5. HOMO-LUMO energy gap, λmax and chemical reactivity indices of 4-amino-2-hydroxy-6-phenylpyrimidine-5-carboxamide by DFT method at B3LYP level using 6-311++G (d, p) as basis sets.

Parameters	Value
E (RB+DFT-LYP) (a.u.)	-794.925
HOMO (eV)	-6.689
LUMO (eV)	-1.857
Energy gap (eV)	4.831
λmax (nm)	256.641
Energy gap (eV)	4.831
Global chemical hardness Ƞ (eV)	2.415
Global chemical Softness σ(eV)	0.413
Electronegativity χ(eV)	4.273
Electronic chemical potential μ (eV)	-4.273
Global electrophilicity index ω (eV)	3.779
Electron affinity A (eV)	1.857
Ionization energy I (eV)	6.689

4.11. Thermodynamic properties

The standard thermodynamic functions such as total thermal .energy (E), total molar heat capacity at constant volume (Cv), total Entropy (S), dipole moment, molar mass and Zero-point vibrational energy (Kcal/mol) has obtained and reported in Table 6.

Table 6. Theoretically computed energy (a.u.), zero-point vibrational energy, (kcal/ mole), rotational constant (GHz), entropy (cal /mole) dipole moment (D) and molar mass (a.m.u.) of 4-amino-2-hydroxy-6-phenylpyrimidine-5-carboxamide by DFT method at B3LYP level using 6-311++G (d, p) as basis sets.

Total E Thermal **Kcal mol-1**	**138.167**
Translational	0.889
Rotational	0.889

Vibrational	136.390
Total (Cv) **Cal mol^{-1}kelvin^{-1}**	55.911
Translational	2.981
Rotational	2.981
Vibrational	49.950
Total entropy (S) **Calmol^{-1}kelvin^{-1}**	119.106
Translational	42.202
Vibrational	32.735
Rotational	44.169
Zero point vibrational energy **Calmol^{-1}**	129.253
Rotational constant (GHz)	0.71360
	0.38644
	0.26984
Dipole moment (D)	1.9338
Molar mass (a. m.u.)	230.080

5. CONCLUSION

The 4-amino-2-hydroxy-6-phenylpyrimidine-5-carboxamide has synthesized and characterized by the FT-IR and 1HNMR spectroscopy. The optimized parameter has computed by DFT method at B3LYP level using 6-311++G (d, p) as basis sets using Gaussian 09W package and Gauss view A-5.0. The vibrational assignments has examined by DFT method of computation has found to be nearly in good agreement with the experimental value of the compound. The absorption maximum of the synthesized molecule has obtained from HOMO-LUMO energy gap.

6. ACKNOWLEDGEMENTS

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